CONFORMATIONAL EFFECTS IN 1,2-DITHIETANE, 1,2-DITHIETE, 1,3-DITHIOLE, 2,3-DIHYDRO-1,4-DITHIIN AND 1,4-DITHIIN RADICAL CATIONS \(^1\)

Glen A. Russell* and Wing Cheung Law
Department of Chemistry
Iowa State University
Ames, Iowa 50011, U.S.A.

Abstract - 1,2-Dithietane radical cations exist in a nonplanar conformation. With trans-3,4-dimethyl substituents, the barrier to ring flip is >5 kcal/mol. Cyclohexene derivatives 7-10 possess a measurable barrier to ring flip. However, the radical cations 11-16 have a much lower barrier and only conformationally time-averaged ESR spectra are observed at -90 °C. The 2,3-dihydro-1,4-dithiin ring of 11 or 19 is conformationally mobile but is locked in a half-chair conformation in 12 and 13.

We have prepared, and where possible studied the effect of temperature, on a series of 1,2-dithietane radical cations (1-6) and a series of radical cations which are cyclohexene-1,2-dithiol derivatives (7-16). These derivatives are representatives of the dithieth (17), 1,3-dithiole (18), 2,3-dihydro-1,4-dithiin (19) and 1,4-dithiin (20) series of radical cations which have been previously described in \(H_2SO_4\) solution.\(^2-4\)
Addition of HSCH₂CH₂SH to H₂SO₄ at room temperature has previously been reported⁴,⁶ to yield a weak signal of 1 (\(a_H = 3.7 \ (4H) \ G, \ g = 2.0193\)). Mono or 1,2-disubstituted derivatives of HSCH₂CH₂SH undergo further oxidation upon treatment with H₂SO₄ to form dithiet e radical cations (e.g., 9, 17 (R = Me)) as the first persistent radical species detectable by ESR spectroscopy. However, reaction of mono or 1,2-disubstituted derivatives of HSCH₂CH₂SH with Al₂Cl₆ in CH₂Cl₂ at 25 °C for 10-30 min leads to persistent ESR signals which we ascribed to the 1,2-dithietane radical cations 2-6 with \(a = 2.0187 \pm 0.0003\). Stereochemistry is maintained with meso-HSCCH(CH₃)CH(CH₃)SH forming 3, \(\text{d}1\)-HSCH(CH₃)CH(CH₃)SH forming 4, \text{cis-c-}C₆H₁₀(SH)₂ forming 5 and \text{trans-c-}C₆H₁₀(SH)₂ forming 6. The ESR hyperfine splittings confirm our previous assumption that 1 exists in a puckered conformation which undergoes a rapid ring flip at room temperature (\(t < 10^{-8}s\)). Derivatives 2-5 from -95 to 25 °C give no evidence of ring inversion, and the results are interpreted in terms of the population of only a single conformation. A consistent interpretation of the hfsc is that in 1 the quasi-axial hydrogens (\(^1H\) and \(^3H\)) have a large hyperfine splitting (\(-7-8 G\)) and that the quasi-equatorial hydrogens (\(^2H\), \(^4H\)) have a small (\(<0.5 G\)) coupling. The magnitude of this interaction reflects the dihedral angle between the C-H bond and the sulfur orbital containing unpaired electron density with an added complication from a 1,3-interaction for the quasi-equatorial hydrogen atoms. Since the SOMO of \(-S\equiv S-\) is antisymmetric, this homohyperconjugation interaction will in effect cancel some part of the 1,2-hyperconjugative interaction for the quasi-equatorial hydrogen atoms.⁴ For the \text{cis-dimethyl} analogue 3, the ESR spectrum is a doublet with \(a_H = 7.6 \ G\) for the quasi-axial hydrogen (\(^3H\)) and \(<0.5 \ G\) for the quasi-equatorial hydrogen atom. The methyl group in the quasi-axial position shows a hfs with \(a = 1.1 \ G\). Alkyl substituents prefer the quasi-axial position since the \text{trans-dimethyl} derivative 4 gives no hfs (\(\Delta H_{1/2} = 2.5 \ G, \) presumably from unresolved Me hfs), and the monomethyl derivative 2 has a resolved hfs for a single hydrogen only (\(a_H = 8.5 \ G\)). Dithietane radical cation 5 has a single quasi-axial hydrogen (relative to the dithietane ring), and the hfsc for \(^1H\) is assigned as 7.6 G. On the other hand, the dithietane radical cation 6 derived from the \text{trans} dithiol exists in a conformation with two quasi-axial hydrogen atoms (the only possible conformation with a chair cyclohexane ring) with \(a_H = 6.30 \ (2H) \ G\).⁷ The radical cation 6 is also detected by ESR in the reaction of cyclohexene with sulfur or S₂Cl₂ in the Al₂Cl₆/CH₂Cl₂ system (Reaction 1).
Radical cations 7-15 possessing the cyclohexene ring were expected to display temperature dependent ESR spectra from the conformation equilibria involving the half-chair cyclohexene conformers. Indeed 7 \((g = 2.0082, \text{prepared by oxidation with } \text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2)\) gave a time-averaged spectrum at -10°C with \(a^H = 10.5 \text{ (4H), 5.8 (4H) G} \) with a coalescence temperature of -70°C and a frozen conformation at -95°C with \(a^H = 14.2 \text{ (2H), 6.8 (2H), 5.8 (4H) G}\); \(\Delta H^\ddagger = 5.6 \text{ kcal/mol, } \Delta S^\ddagger = 3.5 \text{ eu}\). Radical cation 8 \((R = \text{1-Pr}, g = 2.0080)\) had a much lower barrier with selective line broadening below -20°C which yielded \(a^H = 9.6 \text{ kcal/mol, } \Delta S^\ddagger = -8.8 \text{ eu}\). The 1,3-dithiole radical cation 10 \((g = 2.0101)\) prepared by \(\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2\) at -30°C displayed the expected line broadening effect with \(a^H\) (axial) = 11.0 (2H), \(a^H\) (equatorial) = 5.5 (2H), \(a^H\) (methylene) = 26.6 (2H) G at -90°C coalescing to a triplet of pentets at -80°C with \(a^H = 8.20 \text{ (4H), 26.6 (2H) G}\) and with \(\Delta H^\ddagger = 6.2 \text{ kcal/mol, } \Delta S^\ddagger = 5.6 \text{ eu}\). At room temperature, 10 decomposed to 9 \((g = 2.0155, a^H = 3.04 \text{ (4H) G})\) which upon cooling below -50°C gave the line broadening expected for a ring flip with \(\Delta H^\ddagger = 6.0 \text{ kcal/mol, } \Delta S^\ddagger = 3.8 \text{ eu}\). Surprisingly, the dihydrodithin and dithin derivatives 11-16 gave no evidence of cyclohexene ring inversion at -95°C in \(\text{CH}_2\text{Cl}_2\) and four equivalent α-hydrogen atoms were observed for the cyclohexene ring (Table 1).

### Table 1. Hyperfine Splitting Constants for 11-16, -95°C in \(\text{CH}_2\text{Cl}_2\)

<table>
<thead>
<tr>
<th>Structure</th>
<th>g-Value</th>
<th>Cyclohexene (a^H) (4H)</th>
<th>Other (a^H) (in Gauss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>2.0080</td>
<td>7.34</td>
<td>6.85 (2H), 2.26 (2H), 0.73 (2H)</td>
</tr>
<tr>
<td>12</td>
<td>2.0082</td>
<td>7.9</td>
<td>6.1 (2H)</td>
</tr>
<tr>
<td>13</td>
<td>2.0082</td>
<td>7.6</td>
<td>7.6 (1H), 1.6 (2H)</td>
</tr>
<tr>
<td>14</td>
<td>2.0088</td>
<td>3.2</td>
<td>2.6 (2H)</td>
</tr>
<tr>
<td>15</td>
<td>2.0092</td>
<td>2.88 (8H)</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>2.0082</td>
<td>4.1</td>
<td>0.95 (2H)</td>
</tr>
</tbody>
</table>

The barrier to cyclohexene ring flip \((I)\) seems to be a function of the C=C=S angle with larger angles giving rise to a lower barrier. Nonbonded interactions between the R group in 7 and 8 and the cyclohexene α-methylene hydrogen atoms also leads to a lower barrier, presumably by destabilizing the ground state more than the transition state for ring flip.
The radical cation of 2,3-dihydro-1,4-dithiin (19) is a cyclohexene derivative and exists in a half-chair structure with $\Delta H^\ddagger = 2.3$ kcal/mol, $\Delta S^\ddagger = -20$ eu (coalescence temperature ~ 70 °C). Similarly, 11 displayed selective line broadening above -10 °C with $\Delta H^\ddagger = 2.3$ kcal/mol, $\Delta S^\ddagger = -20$ eu for the heterocyclic ring only. The half-chair structure for the dihydro-1,4-dithiin ring (11) with a large hfs by the quasi-axial hydrogen atom ($^1H$) is firmly established by the observation that 12 has a large hfsc for two cyclohexane hydrogen atoms (III), but 13 has a large $\alpha$-coupling to only one cyclohexane hydrogen atom in the quasi-axial position relative to the heterocyclic ring (IV).

The 2,3-dimethyl-1,4-dithiepin derivative 21 has also been synthesized (Reaction 2). The $\alpha$-methylene hydrogens have $\alpha^H = 5.3$ (2H) and 1.85 (2H) G, coalescing at ~ 60 °C with $\Delta H^\ddagger = 5.8$ kcal/mol, $\Delta S^\ddagger = -9.5$ eu.

$$\text{PhH} \xrightarrow{\text{p-MeC}_6\text{H}_4\text{SO}_3\text{H}} \quad \text{H}_2\text{SO}_4 \text{ or } \text{Al}_2\text{C}_6\text{H}_5/\text{CH}_2\text{Cl}_2 \quad 21 \quad (2)$$

REFERENCES AND NOTES

1. Application of Electron Spin Resonance to Problems of Structure and Conformation. 35. This work was supported by grants CHE-8119343 and CHE-8415450 from the National Science Foundation.


7. The only resolved hfs for 5 and 6 are the 7.6 G doublet and 6.3 G triplet, respectively.


9. Based upon the assumption that $\alpha^H (\text{axial}) = 2 \alpha^H (\text{equatorial}).$

Received, 19th August, 1985